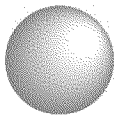


Rubber Manufacturers Association & The International Carbon Black Association Meeting with the California Office of Environmental Health Hazard Assessment

April 28, 2016

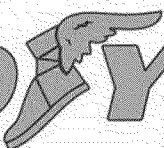


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COOPERTIRES

GOODYEAR  **YEAR**
MORE DRIVEN

KUMHO TIRE ^{1*}
Better, All-Ways

 **MICHELIN**
A better way forward

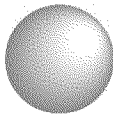
PIRELLI

◆ **SUMITOMO RUBBER NORTH AMERICA, INC.** *

TOYO TIRES®
driven to perform®

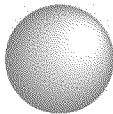
 **YOKOHAMA**

*New members as of 4/20/2016



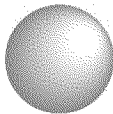
Objectives

- Provide an overview of the types of synthetic rubber used in tire manufacturing
- Provide additional information about the roll and use of antioxidants, antiozonants and accelerators
- Provide additional information about the use of silica and carbon black in tires and how these materials becomes chemically bound in the rubber matrix



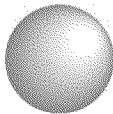
Synthetic Polymers in Tires

- Styrene-Butadiene rubber – most widely used synthetic polymer
- International Institute of Synthetic Rubber Products (IISRP) surveyed their members for information of residual Butadiene and Styrene
 - Butadiene – Mainly non-detect, a few detects at 1 ppm level
 - Styrene – 200-250 ppm from a limited sample



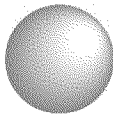
Synthetic Polymers in Tires

- Butadiene
 - Boiling point of Butadiene = 24.08 degrees Fahrenheit
- Styrene
 - Boiling point of Styrene = 293 degrees Fahrenheit
- Mixing, Extrusion, Calendering temperature – 80 – 120 Degrees Fahrenheit
- Tire curing temperature = 302 – 356 Degrees Fahrenheit



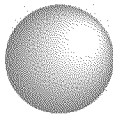
Antioxidants

- Impact of oxidation on Tires:
 - Oxidation causes rubber to either harden or soften
 - Changes in oxidation dramatically affect service life
 - Oxidation causes rubber crosslink chains to be broken



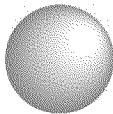
Antioxidants

- Role of Antioxidants in tires:
 - Ensure that changes in tire properties, achieved through compounding and curing, are minimized during service life
 - All tires are compounded to prevent degradation by adding antioxidants



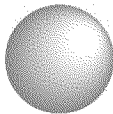
Antiozonants

- Role of Antiozonants in tires:
 - Ozone in the atmosphere causes most rubbers to crack if they are stretched
 - Ozone cracking can be prevented by adding a chemical antiozonant
 - Antiozonants bloom at the surface of the tire to form a protective barrier against ozone to prevent cracking



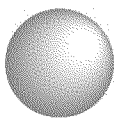
Common Antioxidants & Antiozonants (2008)

- Heterocyclic compounds; such as, TMQ (2,2,4-Trimethyl-1,2-dihydroquinoline),
- TMDQ (Trimethyl-1,2-dihydroquinoline);
- Phenylene-diamine derivatives; such as, IPPD (N-Isopropyl-N'-phenyl-p-phenylenediamine),
- 6PPD (N-1,3-dimethyl-butyl)-N'- phenyl-p-phenylenediamine),



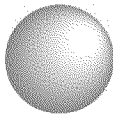
Common Antioxidants & Antiozonants (2008)

- DTPD (N,N'-Ditolyl-p-phenylenediamine),
- DPPD (N,N'-Diphenyl-p-phenylenediamine),
- 77PD (N,N'-Bis(1,4-dimethylpentyl)p-phenylenediamine)
- ADPA (Acetone-diphenylamine condensation product), Phenolic stabilizers, such as BPH (2,2-Methylene-bis-(4-methyl-6-tert-butylphenol) and BHT (2,6-Di-tert-butyl-4-methylphenol)



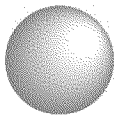
Accelerators or Vulcanizing Agents

- Vulcanization – Changes the physical properties of rubber
 - Increases viscosity, hardness, strength, abrasion resistance
- Uncured rubber is an entanglement of high molecular weight hydrocarbon chains, flows on standing, does not retain its shape
- Curing permanently links together the hydrocarbon chains - Increases strength and transforms sticky black rubber into a solid article

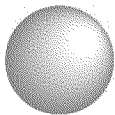


Accelerators or Vulcanizing Agents

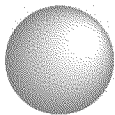
- Role of Accelerators
 - Accelerators
 - Shorten the vulcanization time
 - Affect the length and number of crosslinks which form



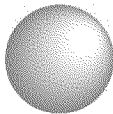
Accelerators or Vulcanizing Agents	Sulphenamides	DCBS (N,N-Dicyclohexyl-2-benzothiazolesulfenamide), TBBS (N-tert-Butyl-2-benzothiazolesulfenamide), CBS (N- Cyclohexyl-2-benzothiazolesulfenamide), MBS (2- morpholinothio) benzothiazole)
	Guanidine derivatives	DPG (N,N'-Diphenylguanidine); DOTG (Di-ortho-tolyl- guanidine)
	Thiazoles	MBT (2-Mercaptobenzthiazole); MBTS (2,2'-Dithiobis(benzothiazole))



Accelerators or Vulcanizing Agents	Dithiophosphates	SDT (Di-(2-ethyl)hexylphosphorylpolysulfide)
	Thiurams	MPTD (Dimethyldiphenylthiuram disulfide)TBTD (tetrabutylthiuram disulfide); TMTD (Tetramethylthiuram disulfide); TMTM (tetramethylthiuram monosulfide),TBZTD (Tetrabenzylthiuram disulfide)



Accelerators or Vulcanizing Agents	Dithiocarbamates	ZDMC (Zn-dimethyldithiocarbamate); ZDEC (Zn-diethyldithiocarbamate); ZDBC (Zn-dibutyldithiocarbamate); ZBEC (Zn-Dibenzylthiocarbamate)
	Thioureas	ETU (Ethylene thiourea); DETU (Diethylthiourea)
	Sulfur donors	DTDM (Dithiomorpholine); DPTT (Dipentamethylenethiuram tetrasulfide); CLD (Caprolactam disulfide); MBSS (2-Morpholinodithiobenzothiazole); OTOS (N-Oxydiethylenedithiocarbamyl-N'-oxydiethylenesulfenamide)



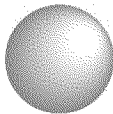
Fillers

Amorphous Silica and Carbon Black

- Nanomaterials
- Modify certain physical properties of the compound
- Their presence in rubber is essential to achieve longer-wearing tires
 - increased tire strength and longevity

Reinforcing Fillers in the Rubber Industry: Assessment as Potential Nanomaterials with a Focus on Tires (September 23, 2011)

<http://www.wbcsd.org/Pages/EDocument/EDocumentDetails.aspx?ID=13861&NoSearchContextKey=true>

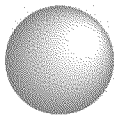


Silica

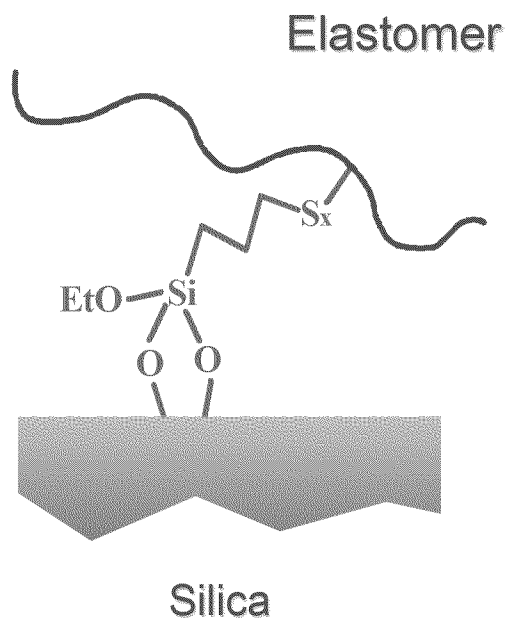
- Why is silica used in tires?
 - Silica – decreases rolling resistance which decreases greenhouse gas emissions of the vehicles using these tires
- Types of silica used in tires
 - Precipitated silica
 - Fumed silica
 - Colloidal silica
 - Reinforcing silica

Reinforcing Fillers in the Rubber Industry: Assessment as Potential Nanomaterials with a Focus on Tires (September 23, 2011)

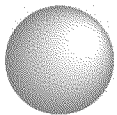
<http://www.wbcsd.org/Pages/EDocument/EDocumentDetails.aspx?ID=13861&NoSearchContextKey=true>



Silica - elastomer bond

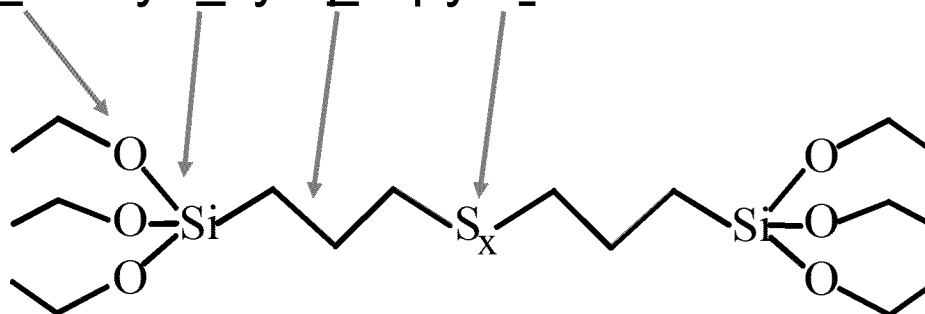


A coupling (SI 69)
agent provides
covalent bonds
between the silica
surface and the
elastomer

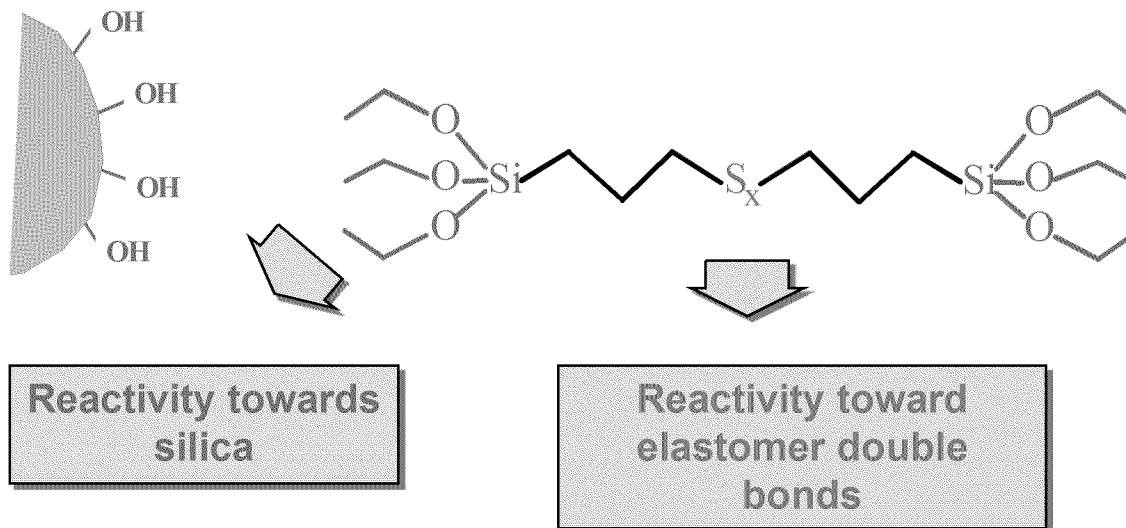


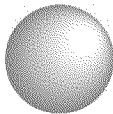
SI69

TESPT : triethoxy silyl propyl tetrasulfide



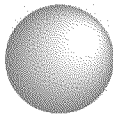
$$X_{\text{avg}} = 4$$





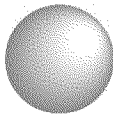
Carbon Black

- Pigment and filler in tires
- Enhances tear strength and improves modulus and wear characteristics of tires
 - The modulus of elasticity is a number that measures an object or substance's resistance to being deformed elastically when a force is applied to it.



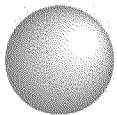
Carbon Black

- Particle Size and Structure Level
 - Particle size or surface area - impacts reinforcement characteristics of a compound
 - Structure of the carbon black inhibits the elasticity of a compound

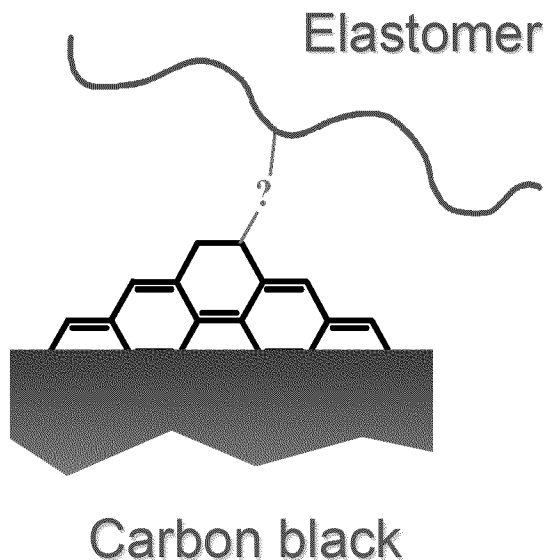


Carbon Black

- How does it become bound in the rubber matrix?
 - Mixing – Necessary to have a high degree of dispersion of the ingredients in the polymer matrix
 - Carbon Black – Particle Size, structure and pellet hardness impact dispersion



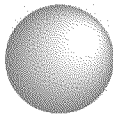
Carbon Black- Filler Interaction



Interface between rigid
(Carbon Black) and soft
(rubber) solid phases

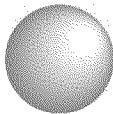
Rubber molecules
adsorbed on the surface of
carbon black physically and
chemically

After mixing and curing some of the rubber is
permanently attached (“bounded”) to the surface of
the carbon black



Bound rubber

- “Rubber portion in uncured rubber that cannot be extracted by a solvent because of the absorption of the rubber molecules onto the filler surface”



Thank you

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